| ![ESRF logo] ESRF | Experiment title: Structural state of 'heavy metals' (Pb, Cd) in bioprecipitated hydrozincite from mine contaminated waters, Sardinia | Experiment number: 08-1-659 |
|---|---|---|
| **Beamline**: BM-08 | **Date of experiment**: from: 08.06.04 to: 11.06.04 | **Date of report**: |
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## Report:

The purpose of the experiment was to investigate, by means of X-ray absorption spectroscopy, the structural state of "heavy metals" associated with bioprecipitated hydrozincite – $Zn_5(CO3)_2(OH)_6$ from metal-contaminated stream waters of Rio Naracauli, Sardinia, Italy. Of specific interest to this experiment were Cd and Pb. Because of the configuration of the beamline at the time of the experiment, upon suggestion by the beamline responsible it was decided to focus the activities mainly on Cd. Materials for the experiment included (Table 1): 1) three natural hydrozincites from the study area; 2) a set of synthetic materials, comprising: commercial $CdCO_3$; Cd-bearing calcite ($CaCO_3$) and four hydrozincites synthesized in Cagliari. Table 1 reports the analytical (ICP-OES) bulk contents of Cd in these materials (for $CdCO_3$, the nominal concentration is shown). Both samples and standards were prepared at the beamline as thin films deposited onto Millipore paper disks, and sealed by Kapton tape. The spectra were collected at the Cd K edge (26711 eV). Both transmission and fluorescence mode were attempted; the best results were obtained in fluorescence mode. To minimize instrumental noise, the chamber was cooled with liquid $N_2$ down to about 80° K. For hydrozincite, the strong fluorescence Zn peak would rapidly lead to detector saturation. Hence, attenuation of the Zn signal was achieved by interposition of an aluminum foil. Because of signal attenuation, and the comparatively low Cd concentration of most samples, spectra collection was relatively lengthy. The experiment was further slowed down by two accidents: 1) main beam failures due to thunderstorms; 2) breakdown of a detector card. The station scientist bypassed the latter problem by setting up data collection in analogic mode instead of digital mode. Because of the above mentioned problems, there was no time, within the allocated shifts, to attempt data collection at the Pb L edge. Spectra were acquired from 26500 to 27500 eV, in 1 to 10 eV steps, counting times 10 to 15 seconds per step. For samples with low counting rates, scans were repeated 2 to 4 times. The overall data acquisition for each sample required 2 to 8 hrs. Representative spectra and transformations are presented in Figs. 1 to 4. A detailed interpretation of the results is currently under way. However, from a first inspection it can be said that: a) the quality of spectra is good, and should provide the basis for meaningful results; in this sense, the experiment can be regarded as successful; b) preliminary analysis indicates that the EXAFS spectra of the natural samples are similar to each other: the following discussion is made considering only the EXAFS spectrum of the sample 20.

The X-ray absorption spectra near the Cd K-edge (Figs. 1 and 2) indicate that the natural sample (20) is similar to sample 11 (hot synthesized Cd-hydrozincite), while it is different from $CdCO_3$. In this latter compound, the Cd atoms are known to occur in a octahedral configuration. The spectra recorded from Cd-

calcite (6) and from cold synthesized Cd-hydrozincite (7) are similar to $CdCO_3$, suggesting that the Cd site in these cases is octahedral. For calcite, this is in agreement with results for Co, Zn, Pb and Ba ions contained as trace elements (Reeder, 1999). Considering the spectra in Fig. 3, one main oscillation is present for the natural sample, while evidence for interatomic coordinations beyond the first shell is found for samples 6, 7, and $CdCO_3$. From the corresponding Fourier transform moduli (Fig. 4; $k^2$-weighed, transformation range = 2.2-9 $Å^{-1}$), the peak of the first shell Cd-O coordination is evident in all the cases. It is worthy noting that: 1) The first shell peak of samples 20 and 11 is shifted of about -0.06Å with respect to the corresponding one of $CdCO_3$ (and of samples 6, 7); 2) The intensity of the first shell peak of the natural sample (20) is similar to that of sample 11. Also in the region 2-4 Å the two signals are similar; 3) The intensity of the first shell peak of the samples 6, 7, $CdCO_3$ is higher than that of the samples 11 and 20; 4) Samples 6, 7 and $CdCO_3$ exhibit interatomic correlations beyond the first shell; the three different peaks typical of $CdCO_3$ in the region 2-4 Å are present also in samples 6 and 7. Moreover, the signal from sample 7 is similar to that of the $CdCO_3$ up to R≅6.5Å. It appears that the local environment around Cd in the natural sample (20) is similar to that of Cd-hydrozincite prepared at high temperature (sample 11); the other compounds present a different Cd site, possibly similar to the octahedral one. Work is in progress to quantify these observations.

Table 1

| Sample (original denomination) | Operational label at ESRF | material | Cd ppm | Cd at. % | Temperature of synthesis |
|---|---|---|---|---|---|
| Cd-calcite Reeder | 6 | Cd-bearing calcite ($CaCO_3$) | 663 | 1.1E-02 | room |
| Cd-idrozincite Reeder | 7 | synthetic Cd-hydrozincite | 41 | 8.5E-04 | room |
| Cd-idrozincite hot | 10 | synthetic Cd-hydrozincite | 261 | 5.4E-03 | ~100° C |
| Cd-idrozincite hot | 11 | synthetic Cd-hydrozincite | 2400 | 5.0E-02 | ~100° C |
| Cd-idrozincite hot | 12 | synthetic Cd-hydrozincite | 20000 | 4.1E-01 | ~100° C |
| ING3 26-06-2001 | 18 | natural hydrozincite | 850 | 1.8E-02 | - |
| ING4 26-06-2001 | 19 | natural hydrozincite | 750 | 1.6E-02 | - |
| ING0N 07-05-1997 | 20 | natural hydrozincite | 540 | 1.1E-02 | - |
| $CdCO_3$ (otavite) synth | $CdCO_3$ | commercial cadmium carbonate | 65% | 20 | Unknown |



Fig. 1



Fig. 2



Fig. 3



Fig. 4